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# SURFACE CORRECTIONS TO BULK ENERGY LOSSES IN
# SCANNING TRANSMISSION ELECTRON MICROSCOPY OF SPHERES

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## Abstract

The interaction of a fast electron penetrating a spherical target is studied, in the frame of the classical dielectric theory. Expressions for $\omega$ the Fourier component of the induced scalar field and energy loss probability are obtained.The reduction in the bulk loss probability due to the surface boundary correction is calculated to all orders in a multipole expansion. The dependence of this correction on the impact parameter and on the radius of the sphere is also studied and compared with the results for films.

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## Introduction

The energy loss experienced by a fast electron interacting with solids has been the subject of continuing interest over the years. In the past few years this interest has been stimulated by the new development and application of the scanning transmission electron microscope (STEM) to the study of small particles (Batson 1982 a,b Cowley 1982, Howie 1983 and Wang and Cowley 1987 a-d). In a typical STEM configuration a well-focused beam ($\approx$0.5 nm) of fast electrons ($\approx$100keV) provides a high resolution scanning image from selected local regions of the sample.

The classical dielectric theory has been widely used to study the energy losses observed in STEM for planar surfaces (Krivanek et al.1983, Howie and Milne 1984,1985).The validity of the assumption of treating the electrons in the beam as point-like classical particles has been established (Ritchie 1981, Ritchie and Howie 1988). The problem of applying this formalism to the study of the energy loss in spheres has been a subject of great interest: the free electron model developed by Fujimoto and Komaki (1968) for the case of a broad beam has been applied to the case of a well focused beam by Schmeits (1981) and Kohl (1983), but only for dipole (l=1) and quadrupole (l=2) excitations.The effect of the size of the probe on the contribution of the first multipoles has been studied by Barberan and Bausells (1985). Using a more general dielectric formalism Batson (1980,1982a,b,1985) has determined the resonance frequencies of small spheres including the effect of surface coating. Ferrell and Echenique (1985) and Echenique et al., (1987 a) have presented a new form of the dielectric model for electron passing outside the sphere, where all multipoles have been considered. A self-energy approach to the interaction of fast electrons with surfaces has been applied to the study of the energy loss for penetrating trajectories (Echenique et al.,1987 b) . These works have established the importance of considering all the multipole terms in order to get a meaningful result. The energy loss in coated spheres for penetrating trajectories has also been studied (Bausells et al., 1987). In a set of papers Wang and Cowley (1987 a-c) have studied, theoretically and experimentally, the case of electrons interacting with spheres embedded in a dielectric support. Tran Thoai and Zeitler (1988 a,b) have studied the energy loss of electrons interacting with spherical targets by using a hydrodynamic model. Recently, Illman et al. (1988) have studied the energy losses spectrum for spheroidal targets.

In this work we evaluate the energy loss probability for the case of an electron passing through a sphere described by a local dielectric function . We neglect retardation effects. We concentrate on the dependence of the bulk correction due to the surface on the geometry of the problem, i.e. to the radius of the sphere and the impact parameter.

## Symbol Table

| | |
|---|---|
| W | Total energy loss |
| $P(\omega)$ | Energy loss probability |
| v | Velocity of the charge |
| $\omega$ | Energy of an elemental excitation. |
| $\omega_p$ | Bulk plasmon energy. |
| $\omega_L$ | Surface plasmon energy. |
| $\varepsilon(\omega)$ | Dielectric response function. |
| $\Phi(r,\omega)$ | $\omega$-component of the field. |
| $\Phi_c(r,\omega)$ | $\omega$-component of the direct Coulomb field. |
| a | Radius of the sphere. |
| s | Impact parameter of the incoming particle. |
| $t = 2a\,\omega_p v^{-1}$ | |
| **r** | Position of the charge. |
| $P_l^{m(x)}$ | Legendre functions. |
| $K_0(x)$ | Bessel function of 0 order. |
| $Ci(x)$ | Cosine integral function. |



Fig. 1. Electron moving at impact parameter s through a dielectric sphere.

## Dielectric formalism

The total energy loss W experienced by a particle of charge q moving on a straight-line trajectory along the z-axis, with constant velocity v, can be obtained in the frame of classical dielectric theory, where the target is described by a dielectric function $\varepsilon(\omega)$. The energy loss is given by:

$$W = - q \int dz \left\{ \frac{\partial \Phi}{\partial z} \right\} \qquad (1)$$

where $\Phi$ is the induced scalar potential evaluated at the charge position.

For the case of a spherical target of radius a, characterized by a dielectric function $\varepsilon(\omega)$, the $\omega$-Fourier component of the total field created by the charge at $r = (r,\theta,\phi)$, moving along the z-axis with constant velocity v (figure 1) may be obtained from standard electrodynamics by means of a multipole expansion imposing continuity conditions to the potential and to the normal component of the displacement. For the case of penetrating trajectories, when the electron is inside the sphere (r<a) we have:

$$\Phi(r,\omega) = \frac{1}{\varepsilon(\omega)} \Phi_c(r,\omega) + \frac{1}{v} \sum_{L\,m} C_{Lm}(\omega) r^L P_L^m(\cos\theta)\,\cos(m\phi) \qquad (2)$$

and for the case of an external electron (r > a), we have:

$$\Phi(r,\omega) = \Phi_c(r,\omega) + \frac{1}{v} \sum_{L,m} D_{Lm}(\omega) \frac{1}{r^{L+1}} P_L^m(\cos\theta)\,\cos(m\phi) \qquad (3)$$
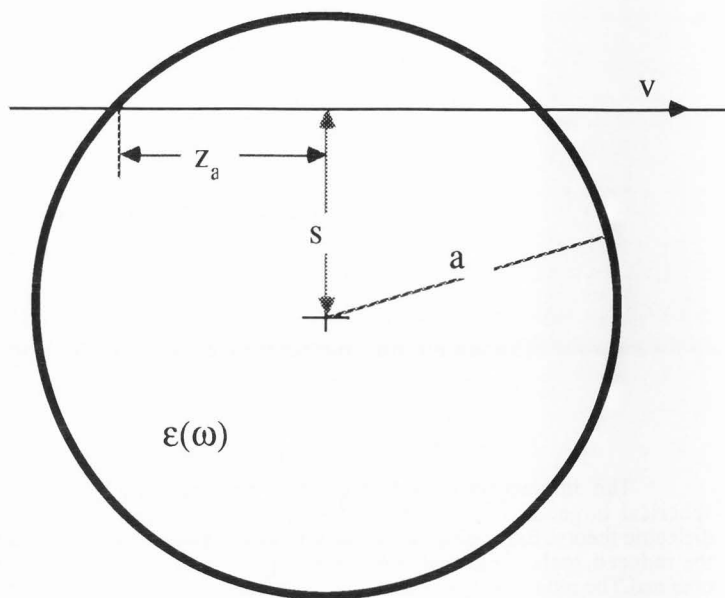
where $\Phi_c(r,\omega)$ is the $\omega$-component of the direct Coulomb potential created by the external charge. ((Explicit expression for $\Phi_c(r,\omega)$ may be found in the work by Echenique et al., (1987 a)). In these expressions $0\leq L\leq \infty$ ; $0\leq m \leq L$ and $P_L^m$ are the Legendre functions. The functions $C_{Lm}(\omega)$ and $D_{Lm}(\omega)$ are given by:

$$C_{Lm}(\omega) = 2(2 - \delta_{m0}) \frac{(L-m)!}{(L+m)!} \; \alpha_L(\omega) \frac{1}{a^L} \{\; B_{Lm}^o(\omega) + B_{Lm}^i(\omega) \;\}$$

$$D_{Lm}(\omega) = 2(2 - \delta_{m0}) \frac{(L-m)!}{(L+m)!} \; a^{L+1} \{\gamma_L(\omega) B_{Lm}^o(\omega) + (\beta_L(\omega)-1) B_{Lm}^i(\omega)\}$$

$$(4)$$

In those expressions $\delta_{m0}$ is the Kronecker delta. $\alpha_L(\omega)$, $\beta_L(\omega)$ and $\gamma_L(\omega)$ are given by:

$$\alpha_L(\omega) = \frac{(L+1)(\varepsilon-1)}{\varepsilon(L\varepsilon+L+1)}$$

$$\beta_L(\omega) = \frac{2L+1}{(L\varepsilon+L+1)}$$

$$\gamma_L(\omega) = \frac{L(1-\varepsilon)}{L\varepsilon+L+1} \qquad (5)$$

The functions $B_{Lm}^{i,o}$ are given by:

$$B_{Lm}^o(\omega) = a^L \int_{z_a}^{\infty} dz \frac{1}{r^{L+1}} P_L^m(\frac{z}{r})\, g_{Lm}(\frac{\omega z}{v})$$

$$B^i_{Lm}(\omega) = \frac{1}{a^{L+1}} \int\limits_0^{z_a} dz\, r^L\, P^m_L(\frac{z}{r})\, g_{Lm}(\frac{\omega z}{v}) \quad (6)$$

where $r=(z^2 + s^2)^{1/2}$ and $z_a=(a^2 - s^2)^{1/2}$. The functions $g_{Lm}(x)$ are $\cos(x)$ if $L+m$ is even or $i^{L+m}\sin(x)$ if $L+m$ is odd.

From expressions (1), (2) and (3) we can evaluate the total energy loss W. The total energy loss may be written as a function of the probability of losing energy $\omega$, $P(\omega)$ (we use atomic units throughout: $m_e=e^2=h/(2\pi)=1$):

$$W = \int\limits_0^\infty \omega\, P(\omega)\, d\omega \quad (7)$$

The contribution to W coming from the potential term $\varepsilon^{-1}\Phi_c(r,\omega)$ in expression (2) is the energy loss experienced by a classical particle travelling a distance $2z_a$ through an infinite medium of dielectric function $\varepsilon(\omega)$, and gives rise to the well-know bulk energy-loss probability:

$$P(\omega) = 4\, z_a \frac{1}{\pi v^2}\, \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\}\, \ln\frac{2v^2}{\omega_p} \quad (8)$$

where $\omega_p$ is the bulk plasmon energy and $\mathrm{Im}(x)$ stands for the imaginary part of x.

The contribution of the surface to the energy loss probability arises from the induced potential terms in expressions (2) and (3). Taking into account the losses along the whole trajectory (i.e., inside and outside the sphere) we get:

$$P(\omega) = \frac{4a}{\pi v^2} \sum_{L,m} (2-\delta_{m,0}) \frac{(L-m)!}{(L+m)!} \left\{ \mathrm{Im}(\gamma_L(\omega))(A^0_{Lm})^2 + \right.$$

$$\left. + \mathrm{Im}(2\beta_L(\omega) - \frac{1}{\varepsilon(\omega)}) A^0_{Lm}A^i_{Lm} + \mathrm{Im}(\alpha_L(\omega))(A^i_{Lm})^2 \right\}$$

$$(9)$$

In this formula functions $A_{Lm}^{i,o}$ are defined: $A_{Lm}^{i,o}= B_{Lm}^{i,o}$ for $L+m$ even and $A_{Lm}^{i,o} =i^{-(L+m)} B_{Lm}^{i,o}$ for odd values of $L+m$. Expression (9) differs from the result reported by Echenique et al., (1987 b) in the bulk term proportional to $\mathrm{Im}(-1/\varepsilon(\omega))$. This difference is due to the fact that in the self-energy formalism, the direct and induced terms of the scalar potential are not clearly visualised in the corresponding terms of the screened interaction. In equation (9) all the bulk terms are included. The term proportional to $\mathrm{Im}(-1/\varepsilon(\omega))$ can be manipulated to exhibit explicitly the dependence on the length of the path inside the sphere. We obtain:

$$\frac{4a}{\pi v^2} \sum_{L,m} (2-\delta_{m,0}) \frac{(L-m)!}{(L+m)!}\, \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} A^0_{Lm}A^i_{Lm} =$$

$$\frac{2}{\pi v^2}\, \mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} \int\limits_0^{2z_a} dz\, Ci(\frac{\omega z}{v})$$
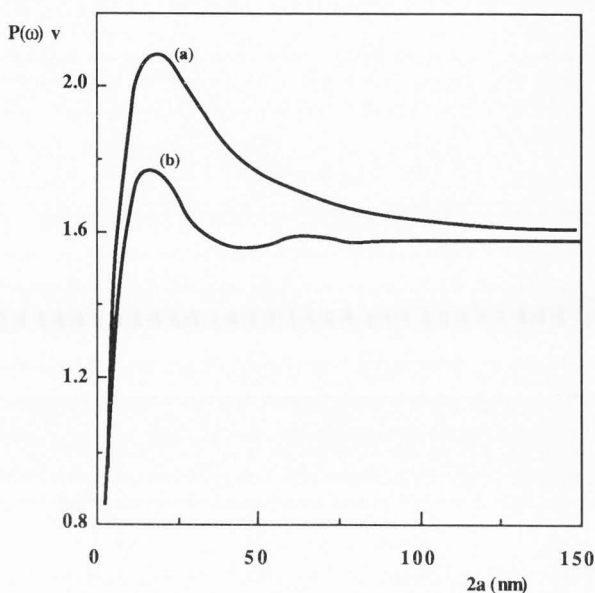
$$(10)$$



Fig.2. Bulk correction to the plasmon excitation probability as a function of the length of the path inside the medium (Al), for 100 keV electrons. Curve (a) corresponds to an electron incident axially on a sphere of radius a. Curve (b) corresponds to a film of thickness 2a. A free electron dielectric response function $\varepsilon(\omega)$ has been used.

where $Ci(x)$ is the cosine integral function.

For a free electron dielectric function $\varepsilon(\omega)= 1-\omega_p^2/\omega^2$, the expression (9) can be written as:

$$P(\omega) = \frac{2a}{v^2} \sum_{L,m} \left\{ \omega_L\delta(\omega - \omega_L) - \omega_p\delta(\omega - \omega_p) \right\}(2-\delta_{m0}) \frac{(L-m)_i}{(L+m)_i} \left\{ A^{i^2}_{Lm} + A^i_{Lm}A^0_{Lm} \right\}$$

$$(11)$$

$$\text{where} \quad \omega_L = \sqrt{\frac{L}{2L+1}}\, \omega_p \quad (12)$$

This expression verifies $P(\omega_p) = - P(\omega_L \rightarrow \omega_p)$. This fact is so-called the begrenzungs effect. It was first derived by Ritchie(1957) in films. (See also Boersch et al. (1968) and Schmeits (1981)).

We now study the dependence of the total bulk correction due to the surface on the radius of the sphere a. We consider an electron incident axially on a sphere described by a free electron dielectric function. For small values of the radius, the behaviour of expression (9) is given by:

$$P(\omega_p) \rightarrow - \frac{t}{v}(1 + \frac{\pi^2}{8} - \gamma - \ln t) = - \frac{t}{v}(1.66 - \ln t) \quad (13)$$

where $t = 2a\omega v^{-1}$. A similar result to this one was first found by Ritchie(1957) for thin films of thickness 2a: $P(\omega_p) = -t.v^{-1}(1.57 -\ln t)$. The bulk term (8) will be generally larger than the bulk correction originated by the presence of the surface. Nevertheless for very small values of the radius a (t<<1, i.e., spheres of a few tenth of nanometers) the

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correction may be larger than the bulk term, in such a way that the total energy loss probability becomes negative. Similar behaviour appears in thin films (Ritchie 1957) and in spheres ( Schmeits,1981). This fact is not very relevant since for targets of atomic dimensions, a macroscopic dielectric response cannot be used to describe the interaction charge-matter.

In figure 2 we plot the bulk correction as a function of the diameter of the sphere for axially incident electrons. In order to get good convergence in the multipolar expansion, a high number of L terms (more than 100) have been taken into account. The dependence of the number of multipolar term required on the radius a has been studied (Echenique et al. 1987 b).The curve obtained is very similar to that corresponding to thin films of the same thickness (Ritchie 1957). The limit of expression (9) for big values of the radius coincides with the thick slab value $P(\omega_p)=\pi/(2v)$.

In figure 3 we show the bulk correction as a function of the radius of the sphere , for several values of the impact parameter. In all cases a maximum appears, approximately when the longitudinal quantification condition for plasmon wavelength is satisfied $2z_a\omega v^{-1} = \pi$. Expression (9) may be used in order to get a qualitative understanding of the oscillations of the bulk energy losses in small spheres reported by Batson (1985). These oscillations may be explained by taken into account the dependence of the bulk correction on the impact parameter s. In figure 4 we plot the bulk correction versus the impact parameter for fixed values of the radius a. In all the cases the bulk correction increases as the impact parameter does. This fact may qualitatively explain the growth of the oscillations with the probe width in the experimental data. Ritchie and Howie (1988) have established that most of relevant effects due to the beam width in STEM may be reproduced by convoluting the results for classical particles with different impact parameters. Therefore, in a spread beam, the contribution to bulk correction of electrons out of the axis tends to increase the total bulk term, as experimental data show. In order to get a conclusive explanation of this effect further theoretical work is needed.

In figure 4, for large radius and for values of s close to a, $P(\omega)$ shows a pronounced peak. This fact may be understood by considering that in these cases, the inner part of the trajectory may be approximated by that of an electron moving parallelly and very close to a plane surface. The bulk terms in the stopping power for this former problem, obtained in the frame of the dielectric theory (Echenique and Pendry (1975); Nuñez et al.(1980)) behave as $K_0(\omega zv^{-1})$, ($K_0$ is the Bessel function, and z the distance to the surface), which diverges logarithmically when $z\rightarrow 0$. In the case of electrons with grazing trajectories such a divergence does not appear due to the fact that for this case the length of the path inside the sphere tends to zero as $s\rightarrow a$ and therefore the energy loss probability remains finite. Echenique (1985) has established for planar symmetry, that the introduction of the k dependence on the medium response, does not substantially change the excitation spectrum but for values of the distance z of a few tenth of nm. These distances are shorter than those where the above peak appears, so one can consider these curves as basically correct.

## Conclusions

For STEM electrons we have calculated For STEM electrons the reduction in the bulk loss probability due to the surface boundary correction, for targets of spherical symmetry to all orders in a multipole expansion. Our results, when all multipoles are taken into account recover the planar limits first derived by Ritchie (1957). A detailed study of the

dependence of the bulk loss probability on both the radius of the sphere and the impact parameter has been presented and can be of guidance to the understanding of Batson's (1985) experimental data. However a complete analysis of this problem requires a calculation taking into account the spatial extension of the electron probe. An extension of our method to the problem of an electron interacting with more complicated geometries such as the one of a supported sphere or semisphere should be undertaken. Such work is in progress in our laboratory.

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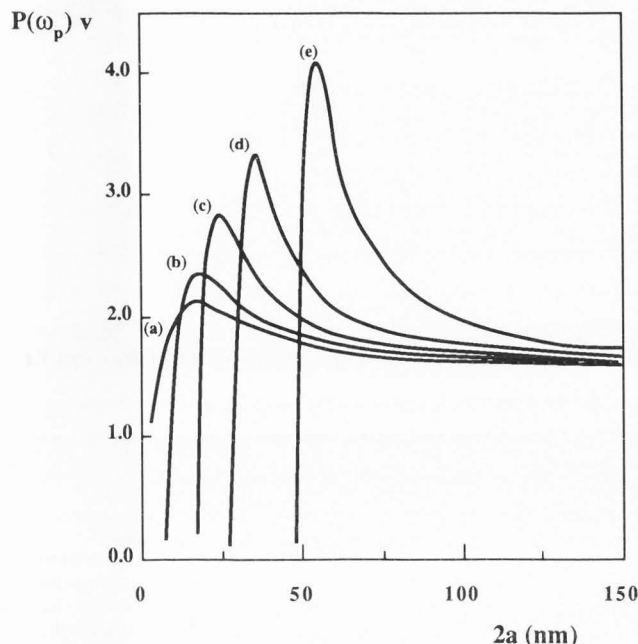
Fig. 3. Bulk correction to the plasmon excitation probability as a function of the radius of an Al sphere for several values of impact parameter for 100 keV electrons. Curve labeled (a)  s=0 nm;  curve (b) s=4.5 nm; curve (c) s=9.5 nm; curve (d) s=14.5 nm and curve (e) s=24.5 nm. A free electron dielectric response function $\varepsilon(\omega)$ has been  used.
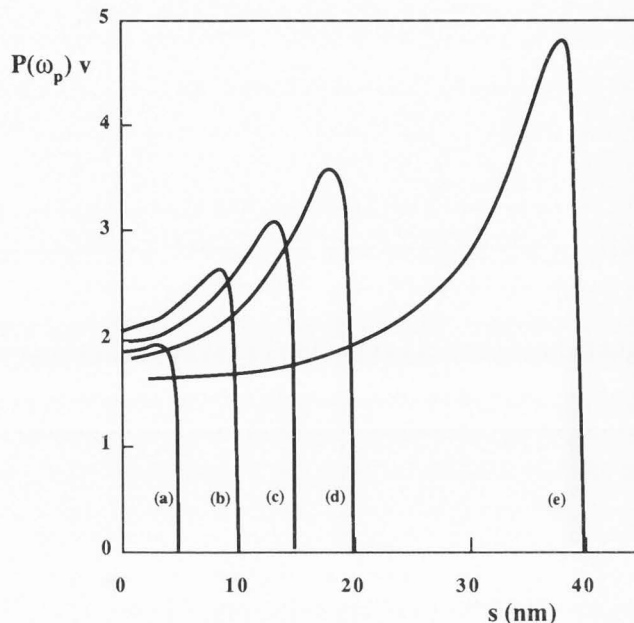
Fig. 4. Bulk correction to the plasmon excitation probability as a function of the impact parameter s for several Al spheres (100 keV). Curve labeled (a)  a=5nm; curve labeled (b) a=10nm.; curve (c) a=15nm; curve (d) a=20nm.; curve (e) a=40nm. A free electron dielectric response function $\varepsilon(\omega)$ has been used.

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### Discussion with Reviewers

**J.M. Cowley:** It is stated that the macroscopic dielectric response can not be used to describe the charge-matter interaction for particles of atomic dimensions: what are the minimum dimensions for which the macroscopic dielectric response may possibly be used?
**Authors:** To our knowledge there is no straightforward answer to this question.  We note however that theoretical studies presented by H. Raether in the book on Plasmons (Springer Tracts in Modern Physics, volume 88) of the response of very thin ( ~5Å) overlayers on bulk dielectric media, show quite reasonable agreement with experiment.

**J.M. Cowley:** Do these mathematical expressions correspond to the generation of plasmons and surface plasmons and if so, what variation of plasmon frequencies are to be expected?
**Authors:** We are calculating the Begrezung effect, i.e. the reduction in the bulk loss probability, due to the surface boundary correction to all orders in the multipole expansion. Note that the bulk loss is expected to occur at the energy $\omega_p$, irrespective of the correction.

**J.M. Cowley:** How do the predictions from your model compare with theoretical and experimental results of Wang and Cowley (e.g. Ultramicroscopy 2,347 (1987))?
**Authors:** Wang and Cowley's unconventional way of solving the Poisson equation leads to a response function $Im(A_{LM})$ (eq. (16) of Ultramicroscopy 21,335,(1987)) in which time and $\omega$ appear together!. We do not see how the wake potential results of Ritchie and coworkers (Phys. Rev.

B20, 2567 (1979)) for an infinite medium, the Ferrell and Echenique result for the energy loss probability for impact parameters greater than the radius of the sphere, could be recovered using Wang and Cowley formalism.

**A.Howie:** Can the authors suggest some practical applications which this theory may have in the field of electron microscopy?

**Authors:** No, unless helping to understand the interaction in this particular geometry in a correct way might be considered "a practical application".